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C_xF_y & NH_3
etching insulating

(54) Title: METHOD OF ETCHING CARBON-CONTAINING SILICON OXIDE FILMS

(57) Abstract: We have discovered a method for plasma etching a carbon-containing silicon oxide film which provides excellent etch profile control, a rapid etch rate of the carbon/containing silicon oxide film, and high selectivity for etching the carbon-containing silicon oxide film preferentially to an overlying photoresist masking material. Then the method of the inention is used, a highter carbon content in the carbon/containing silicon oxide film results in a faster etch rate, at least up to ta carbon content of 20 atomic percent. In particular, the carbon-containgin silicon oxide film results in a faster etch rate, at least up to a carbon content of 20 atomic percent. In particular, the carbon containg silicon oxide film is plama etched using a plama generated from source gas comprising NH_3 and C_xF_y. It is necessary to achieve the proper balance between the relative amounts of NH_3 and C_xF¿y ?in the plasma source gas in order to provide a balance between etch by/product polymer deposition and removal on various surfaces of the substrate being etched. The NH¿3 ?gas functions to "clean up" deposited polzmer on the photoresist surface, on the etched surface, and on process chamber surfaces. The atomic ratio of carbon: nitrogen in the plasma source gas typically ranges from about 0.3:1 to about 3:1. We have found that C_2F_6 and C_4F_8 provide excellent etch rates during etching of carbon-containing silicon oxide films.

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METHOD OF ETCHING CARBON-CONTAINING SILICON OXIDE FILMS

BACKGROUND OF THE INVENTION

1. Field of the Invention

The present invention pertains to etching of carbon-containing silicon oxide films.

2. Brief Description of the Background Art

Low k dielectric materials are the trend for the next generation of dielectric materials used in semiconductor manufacture. The term "low k dielectric" typically refers to any material having a dielectric constant (k) value lower than that of silicon dioxide ($k \approx 4.0$). There are many different kinds of low k dielectric materials, including organic polymer-based materials, as well as silicon oxide-based materials which contain additives such as fluorine, carbon, and hydrogen.

Various methods for producing carbon-containing silicon oxide films are known in the art. U.S. Application Serial No. 09/021,788, of Yau et al., and German Patent No. DE 19654737, of Itoh et al., for example, disclose methods for producing such films. In particular, the '788 application discloses a method for depositing a low dielectric constant film by reacting an organosilane compound (such as methyl silane, CH_3SiH_3) with an oxidizing gas (such as N_2O or O_2). During deposition of the film, methyl (CH_3) groups bond to the silicon oxide structure. The presence of carbon in the film causes a reduction in the dielectric constant of the film.

Plasma etching of silicon oxide films is typically performed using a source gas containing a C_xF_y gas, such as CF_4 or C_2F_6. The carbon and fluorine in the source gas are typically sufficient to provide an acceptable etch rate for the silicon oxide. However, for carbon-containing silicon oxide films, etching cannot proceed very far when C_xF_y is used as the sole etchant gas. The carbon in the film, together with the carbon and fluorine in the

plasma source gas, combine to produce undesirable long-chain carbon-fluorine polymers which deposit over surfaces of the semiconductor structure being etched, hampering the etching process. The long-chain carbon-fluorine polymers also contaminate surfaces within the process chamber.

Prior art solutions to this problem have included adding a source of oxygen to the C_xF_y gas. The oxygen reacts with the carbon in the carbon-containing silicon oxide film, preventing undue polymer deposition and increasing the etch rate of the film. However, oxygen also attacks the overlying photoresist layer, which is typically used as a patterning mask for underlying feature (such as a contact via) etching. Therefore, although the presence of oxygen improves the etch rate of the carbon-containing silicon oxide film, the selectivity for etching the silicon oxide film in preference to an overlying photoresist layer is reduced.

It would be desirable to provide an effective method for etching carbon-containing silicon oxide films that would provide both an acceptable etch rate and acceptable selectivity for etching the silicon oxide film relative to an overlying photoresist layer.

SUMMARY OF THE INVENTION

We have discovered a method for plasma etching a carbon-containing silicon oxide film which comprises exposing the film to a plasma generated from a source gas comprising NH_3 and C_xF_y. The carbon-containing silicon oxide film generally comprises less than about 20 atomic percent carbon; typically the carbon content ranges from about 8 to about 20 atomic percent carbon; more typically, the carbon content ranges from about 8 to about 13 atomic percent carbon. The carbon-containing silicon oxide film frequently contains hydrogen. When hydrogen is present, the hydrogen concentration is generally less than about 45 atomic percent of the overall film composition. Typically the hydrogen

concentration ranges from about 30 to about 45 atomic percent; more typically, the hydrogen content ranges from about 30 to about 40 atomic percent of the carbon-containing silicon oxide film.

Active fluorine species in the etchant plasma react with silicon in the carbon-containing silicon oxide film (substrate). Oxygen species generated from the carbon-containing silicon oxide film and hydrogen species from the plasma react with carbon. The method of the invention provides excellent etch rates, as well as superior etch selectivity for the carbon-containing silicon oxide layer in preference to an overlying photoresist masking material. It is our opinion, but not by way of limitation, that etch selectivity is improved because a layer of polymer (generated from the C_xF_y in the plasma source gas) is deposited upon the upper surface of the photoresist masking layer during the etching process. This layer of deposited polymer protects the photoresist from being consumed during the silicon oxide etching process. Simultaneously, the ammonia (NH_3) gas portion of the plasma source gas functions to "clean up" deposited polymer on the photoresist surface, on the etched surface, and on the process chamber surfaces. It is necessary to achieve the proper balance between the C_xF_y and NH_3 in the plasma source gas in order provide a balance between by-product polymer deposition and removal on various surfaces of the substrate being etched. Oxygen may be added to the plasma source gas to increase the etch rate of the carbon-containing silicon oxide, but this reduces the selectivity in favor of etching of the carbon-containing silicon oxide relative to the photoresist.

Carbon and nitrogen are typically present in the source gas in an atomic ratio within a range of about 1 : 0.3 to about 1 : 3 of carbon : nitrogen; preferably, within a range of about 1 : 0.7 to about 1 : 2.2 of carbon : nitrogen; and more preferably, within a range of about 1 : 1 to about 1 : 1.8.

The method of the invention comprises exposing the carbon-containing silicon oxide

film to a source gas comprising NH_3 and C_xF_y, where x ranges from about 1 to about 6 and y ranges from about 4 to about 8. Typically, x = 2 to 4 and y = 4 to 8. In particular, we have found that C_2F_6, C_4F_6, C_4F_8, and C_5F_8 provide excellent etch rates and etch selectivity.

Although less preferred, the plasma source gas may further include a non-reactive, diluent gas selected from the group consisting of argon, helium, xenon, krypton, and combinations thereof.

The method of the invention for etching carbon-containing silicon oxide films has provided etch rates of at least 2.2 μm per minute and etch selectivity relative to an overlying photoresist layer of up to about 25 : 1. This combination of rapid etch rate of the carbon-containing silicon oxide with high etch selectivity relative to the photoresist masking layer was unexpected. Also important is the clean process chamber surface after completion of etch.

BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 shows an IPS™ etch process chamber 100 of the kind used during the generation of the data illustrated in Figure 2.

Figure 2 shows the effect of changes in C_4F_8 and NH_3 gas feed rates to the plasma on the profile taper of an etched contact via; the etch selectivity, in terms of preference for etching carbon-containing silicon oxide relative to photoresist masking material; the etch rate of photoresist masking material; and the etch rate of carbon-containing silicon oxide.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

Described in detail below is a method of etching a carbon-containing silicon oxide film. The method involves exposing the film to a plasma generated from a source gas comprising NH_3 and C_xF_y.

As a preface to the detailed description, it should be noted that, as used in this specification and the appended claims, the singular forms "a", "an", and "the" include plural referents, unless the context clearly dictates otherwise.

I. AN APPARATUS FOR PRACTICING THE INVENTION

Figure 1 shows an example of an apparatus which can be used to practice the method of the invention, the Applied Materials IPS™ dielectric etch chamber (designated by reference numeral 100). The IPS™ chamber 100 includes two plasma power sources, provided by an outer coil 102 (frequency tuned at 2.0 $\pm$ 0.1 MHZ) and an inner coil 104 (frequency tuned at 2.3 $\pm$ 0.1 MHZ). A substrate (not shown, but typically a silicon wafer) is held to a support platform, which is typically a ceramic electrostatic chuck 108. A bias voltage may be applied to substrate support platform 108 by means of bias power source 106 (frequency tuned at 1.7 $\pm$ 0.2 MHz). Plasma source gas is fed into the etch chamber from a location 110 which is beneath the substrate and moves toward the upper portion of etch chamber 100, where a plasma is generated. The method of the invention is preferably performed in an apparatus having separate power controls for the plasma source power and substrate bias power.

Although the above apparatus provides excellent results, it is expected that the method can also be carried out in other apparatus of various kinds known in the art, including, but not limited to, RF generated parallel plate; electron cyclotron resonance (ECR); high-density reflected electron, helicon wave, inductively coupled plasma(ICP) and transformer coupled plasma (TCP) apparatus. Examples of such processing apparatus are described in U.S. Patent Nos. 6,095,084; 6,077,384; 6,074,512; 6,071,372; 6,063,233; 6,054,013; 6,036,878; 6,026,762; 6,020,686; 5,976,308; and 5,900,064, each of which is hereby incorporated by reference.

II. THE METHOD OF THE INVENTION FOR ETCHING A CARBON-CONTAINING SILICON OXIDE FILM

The present invention pertains to etching of carbon-containing silicon oxide films. Typically, the films consist of methyl (CH_3) groups bonded to a silicon oxide structure. Carbon is generally present at less than about 30 atomic percent. Typically, the carbon content is within a range of about 8 to about 20 atomic percent; more typically, within the range of about 8 to about 13 atomic percent, of the silicon oxide film. The carbon content of the silicon oxide film is important because it affects both the general mechanical properties of the film and the conductivity of the film.

Hydrogen is also frequently present in the carbon-containing silicon oxide film. Generally, the hydrogen concentration is less than about 50 atomic percent. Typically, the hydrogen content is within a range of about 30 to about 45 atomic percent of the silicon oxide film.

The method of the invention comprises exposing the carbon-containing silicon oxide film to a plasma generated from a source gas comprising NH_3 and C_xF_y. Carbon and nitrogen are typically present in the plasma source gas in an atomic ratio within the range of about 0.3 : 1 to about 3 : 1 of carbon : nitrogen; preferably, within the range of about 0.5 : 1 to about 1.4 : 1 of carbon : nitrogen; most preferably, within the range of about 0.6 : 1 to about 1 : 1 of carbon : nitrogen. With reference to the C_xF_y gas, x typically ranges from about 1 to about 6, and y typically ranges from about 4 to about 8. The C_xF_y gas is typically selected from the group consisting of C_2F_6, C_3F_6, C_4F_6, C_4F_8, C_5F_8, and combinations thereof. In particular, we have found that C_2F_6 and C_4F_8 provide excellent etch rates and etch selectivity.

The plasma source gas may further include oxygen in order to increase the etch rate of the carbon-containing silicon oxide film. However, oxygen should comprise no more than about 30 volume % of the source gas, and typically less than about 20 volume %, as the

presence of oxygen may compromise the selectivity for etching the carbon-containing silicon oxide film relative to an overlying photoresist layer.

Although less preferred, the plasma source gas may further include a non-reactive, diluent gas selected from the group consisting of argon, helium, xenon, krypton, and combinations thereof.

Typical process conditions for etching a carbon-containing silicon oxide film according to the method of the invention, when the power supply is controlled separately for the plasma source power and the substrate bias power, are presented in Table One, below. In cases where there is only a single plasma source power, the "Inner (W)" source power value is simply "0 W".

Table One. Preferred Embodiment Process Conditions for Etching Carbon-containing Silicon Oxide Films

Process Parameter	Preferred Process Conditions	More Preferred Process Conditions	Most Preferred Process Conditions
NH_3 Flow Rate (sccm)	50 - 150	75 - 125	75 - 100
C_xF_y Flow Rate (sccm)	10 - 30	15 - 25	18 - 25
O_2 Flow Rate (sccm)	0 - 30	0 - 20	0 - 10
Ar Flow Rate (sccm)	0 - 1000	0 - 800	0 - 500
Plasma Source Power* - Outer (W)	800 - 2000	800 - 1600	1000 - 1600
Plasma Source Power* - Inner (W)	0 - 1000	0 - 600	0 - 500
Substrate Bias Power** (W)	600 - 1800	600 - 1500	800 - 1200
Substrate Bias Voltage (-V)	200 - 1000	200 - 800	400 - 700
Process Chamber Pressure (mTorr)	10 - 60	20 - 40	30 - 40
Substrate Temperature (°C)	-15 - +15	-15 - +15	-15 - +15

* The term "source power" refers to the power that is responsible for sustaining the plasma by providing a major portion of the energy to create active etchant species in the process chamber.

** The term "bias power" refers to the power applied to the substrate support platen to produce a negative voltage on the substrate surface. Typically, the negative voltage is used to control high energy species bombardment and the directionality of ions toward a substrate.

During the development of the present method for etching carbon-containing silicon oxide films, we performed several experiments to optimize the plasma source gas composition and etch process conditions. The experiments were all performed in an Applied Materials IPS™ dielectric etch chamber, as shown in Figure 1. The results of these developmental experiments are presented in Table Two, below. The use of an IPS™ dielectric etch chamber having both an outer plasma source power and an inner plasma source power provided unusually high uniformity of etch across the substrate (wafer) surface.

Table Two. Carbon-Containing Silicon Oxide Film Etching Method, Developmental Data

Run #	1	2	3	4	5	6	7	8
NH_3 (sccm)	100	100	100	70	70	70	70	70
C_4F_8 (sccm)	25	25	25	25	18	25	28	25
Ar (sccm)	--	--	100	--	--	--	--	--
Proc. Chamber Pressure (mTorr)	60	40	40	40	40	40	40	30
Source Power (W)*	1600	1600	1600	1200	1200	1200	1200	1200
Bias Power (W)	1200	1200	1200	1000	1000	850	1000	1000
Substrate Temp. (°C)**	60	60	60	60	60	60	60	60
SiO_2 Etch Rate (μm/min)	3.1	2.4	2.2	2.6	2.8	2.5	2.6	2.2
SiO_2: PR*** Etch Selectivity	4.1 : 1	2.0 : 1	2.9 : 1	16 : 1	6.3 : 1	25 : 1	16 : 1	13 : 1
Etch Profile	Tapered	Striation	Slight bowing	Vertical	Vertical	Vertical	Vertical	Bowing

* This source power is a combination of the outer source power and the inner source power, where the ratio of the outer source power to the inner source power averaged about 2 : 1.

** This substrate temperature value is ± 20 °C. Typically the temperature of the cathode upon which a wafer sets is about 10 °C, and the wafer temperature is about 50 °C higher, depending on the particular process operating conditions.

*** PR = Photoresist. The term "selectivity" is used to refer to the ratio of the etch rate of the SiO_2 to the etch rate of the photoresist.

Under the process conditions indicated above, where the chamber pressure was about 40 mTorr or less, the plasma density in the etch chamber during etching was estimated to range from about 5×10^{11} e^-/cm^3 to about 5×10^{12} e^-/cm^3.

Etch rates for the carbon-containing silicon oxide films ranged from 2.2 to 3.1 μm per minute. (In general, an etch rate of at least 0.8 μm per minute is considered acceptable.) Run #1 showed the highest etch rate, 3.1 μm per minute. The atomic ratio of carbon : nitrogen in the plasma source gas in Run # 1 was 1 : 1, with a relatively high process chamber pressure (60 mTorr), source power (1600 W), and bias power (1200 W).

Typically, a patterned photoresist layer is used as a mask to etch a feature in an underlying layer of carbon-containing silicon oxide. The term "feature" refers to, but is not limited to, interconnects, contacts, vias, trenches, and other structures which make up the topography of the substrate surface. A UV-5 photoresist manufactured by Shipley Co., Massachusetts, USA, was used in the development runs listed in Table Two. The photoresist layer had a thickness of about 8000 Å.

It is desirable that the photoresist masking layer be consumed at a much lower rate than the underlying layer which is being etched, that is, the etch selectivity for the carbon-containing silicon oxide relative to the photoresist should be high (typically, at least 5 : 1). Run #6 showed the highest silicon oxide : photoresist etch selectivity, 25 : 1. Run #6 utilized an atomic ratio of 1.4 : 1 carbon : nitrogen in the plasma source gas, with a lower process chamber pressure (40 mTorr) and source power (1200 W). Run #6 also utilized the lowest bias power (850 W) out of all of the runs.

The best etch profile was also achieved in Run # 6. The term "etch profile" (or "feature profile") generally refers to, but is not limited to, the cross-sectional profile of an etched feature. In many instances herein, where the etched feature pattern is one of trenches etched within a substrate, the etch profile is described in terms of an angle between the trench sidewall and a horizontal line drawn along the bottom of the trench at the base of the trench. The term "vertical profile" refers to an etched trench profile where the trench sidewall is essentially perpendicular to the horizontal line drawn along the bottom of the

trench. Frequently the angle between a line drawn along the trench sidewall and the horizontal line along the bottom of the trench is about 88° and 90° (or 90° to about 92°, depending on the direction from which the angle is measured). The term "undercut profile" refers to a trench sidewall profile where the width of the trench increases as the distance away from the opening at the top of the trench increases. The term "tapered profile" refers to a trench sidewall profile where the width of the trench decreases as the distance away from the opening at the top of the trench increases. A"bowed profile" is one in which the width of the trench is smaller at the top of the trench, enlarged as the trench goes deeper into the substrate, and then smaller again at the bottom of the trench.

The addition of argon to the plasma source gas in Run #3 resulted in a lowered etch rate (2.2 μm per minute), as well as a reduced silicon oxide : photoresist etch selectivity (2.9 : 1). Further, the etch profile obtained in Run #3 showed a slight bowing, that is, the width of the cross-section of the feature was largest approximately midway between the opening on the substrate surface and the bottom of the feature.

Overall, Run #6 provided the best results in terms of etch rate, etch profile, and selectivity for etching the silicon oxide layer relative to the overlying photoresist layer.

As demonstrated by the results presented in Table Two, above, the method of the invention provides excellent etch rates, as well as superior selectivity for etching a carbon-containing silicon oxide film relative to an overlying photoresist layer.

Figure 2 shows the effect of changing the relative amounts of C_4F_8 relative to NH_3 in a plasma source gas, when the other process variables were held constant as follows: The outer source power was 800 W at 2 MHZ ; the inner source power was 400 W at 2 MHZ; the bias power was 1000 W at 1.7 MHZ; the process chamber pressure was 40 mTorr; and the substrate temperature was within the range of 60 - 100°C, most commonly at about 60 °C. Fifteen (15) Torr of helium back pressure was used against the backside of the

substrate wafer to assist in heat transfer. The electrostatic chuck was water-cooled.

The scale labeled 202 in Figure 2 shows the flow rate ranges for C_4F_8 in sccm, while the scale labeled 204 in Figure 2 shows the flow rate ranges for NH_3.

The graphs 210 show the change in etched wall profile from vertical as a function of changes in the flow rates of C_4F_8 and NH_3. The profile is shown to change from about 0° to about 4°, where an increase in C_4F_8 causes a decrease in profile undercut, while an increase in NH_3 causes an increase in profile undercut.

The graphs 220 show the change in etch selectivity (etch rate ratio of carbon-containing silicon oxide : photoresist masking material) as a function of changes in the flow rates of C_4F_8 and NH_3. The selectivity is shown to change from about 5.2 to about 8.7, where an increase in C_4F_8 causes an increase in selectivity, while an increase in NH_3 causes a decrease in selectivity.

The graphs 240 show the change in photoresist masking material etch rate as a function of changes in the flow rates of C_4F_8 and NH_3. The etch rate is shown to vary from about 3300 Å per minute to about 4300 Å per minute, where an increase in C_4F_8 causes a decrease in photoresist etch rate, while an increase in NH_3 causes an increase in etch rate.

The graphs 260 show the change in carbon-containing silicon oxide layer etch rate as a function of changes in the flow rates of C_4F_8 and NH_3. The etch rate is shown to vary from about 22,500 Å per minute to about 27,500 Å per minute, where an increase in C_4F_8 causes no apparent change in the carbon-containing silicon oxide layer etch rate, while an increase in NH_3 causes a decrease in the etch rate. As shown in graph 260, changing the flow rate of either C_4F_8 or NH_3 had minimal impact on the etch rate of the carbon-containing silicon oxide film.

In summary, the relative amounts of C_xF_y and NH_3 need to be carefully balanced in order to maintain a vertical etch profile while providing high selectivity for etching carbon-

containing silicon oxide relative to a photoresist masking material. Based on a series of experiments in which the carbon content of silicon oxide films was varied from 0 up to about 20%, we have also determined that films containing higher carbon concentrations have a higher etch rate when etched according to the method of the invention.

The above described preferred embodiments are not intended to limit the scope of the present invention, as one skilled in the art can, in view of the present disclosure expand such embodiments to correspond with the subject matter of the invention claimed below.

CLAIMS

We claim:

1. A method of etching a carbon-containing silicon oxide film comprising exposing said silicon oxide film to a plasma generated from a source gas comprising NH_3 and C_xF_y.

2. The method of Claim 1, wherein said carbon-containing silicon oxide film comprises less than about 30 atomic percent carbon.

3. The method of Claim 1, wherein said carbon-containing silicon oxide film further comprises hydrogen, at a concentration of less than about 50 atomic percent hydrogen.

4. The method of Claim 1, wherein an atomic ratio of carbon : nitrogen in said source gas is less than about 3 : 1.

5. The method of Claim 1, wherein an atomic ratio of carbon : nitrogen in said source gas ranges from about 0.5 : 1 to about 1.4 : 1.

6. The method of Claim 5, wherein an atomic ratio of carbon : nitrogen in said source gas ranges from about 0.6 : 1 to about 1 : 1.

7. The method of Claim 1, wherein x ranges from about 1 to about 6, and y ranges from about 4 to about 8.

8. The method of Claim 7, wherein $x = 2 - 5$ and $y = 6 - 8$.

9. The method of Claim 8, wherein said C_xF_y gas is selected from the group consisting of C_2F_6, C_3F_6, C_4F_6, C_4F_8, C_5F_8, and combinations thereof.

10. The method of Claim 9, wherein said C_xF_y gas is selected from the group consisting of C_2F_6 and C_4F_8.

11. The method of Claim 1, wherein said source gas further comprises O_2, at a concentration of less than about 30 volume %.

12. The method of Claim 1, wherein said source gas further comprises a non-reactive, diluent gas selected from the group consisting of argon, helium, xenon, krypton, and combinations thereof.

13. The method of Claim 1, wherein said carbon-comprising silicon oxide film is etched at a rate of at least 1.5 μm per minute.

14. The method of Claim 1, wherein the ratio of an etch rate of said carbon-comprising silicon oxide film relative to an etch rate of an overlying photoresist layer is at least 10 : 1.

15. The method of Claim 1, wherein a substrate bias voltage within the range of about -200 V to about - 1000 V is applied during the performance of said method.

16. The method of Claim 1, wherein a plasma density within a substrate processing area during performance of said method is within a range from about 5 x 10^{11} e^-/cm^3 to about 5 x 10^{12} e^-/cm^3.

17. The method of Claim 1, wherein a total source power applied during performance of said method ranges from about 800 W to about 2000 W.

18. A method of etching a carbon-containing silicon oxide film comprising exposing said silicon oxide film to a plasma generated from a source gas comprising NH_3 and C_xF_y, wherein an atomic ratio of carbon : nitrogen in said source gas is less than about 3 : 1, wherein said carbon-containing silicon oxide film resides on a substrate which is biased to within a range of about - 200 V to about - 1000 V, and wherein a plasma source power is applied using one device which is external and one device which is internal to a process chamber in which said etching is carried out.

19. The method of Claim 18, wherein a sum of said plasma source power applied is within a range from about 800 to about 3,000 W.

20. The method of Claim 19, wherein the ratio of plasma source power applied using said device which is external : plasma source power applied using said device which is internal is 2 : 1 or higher.

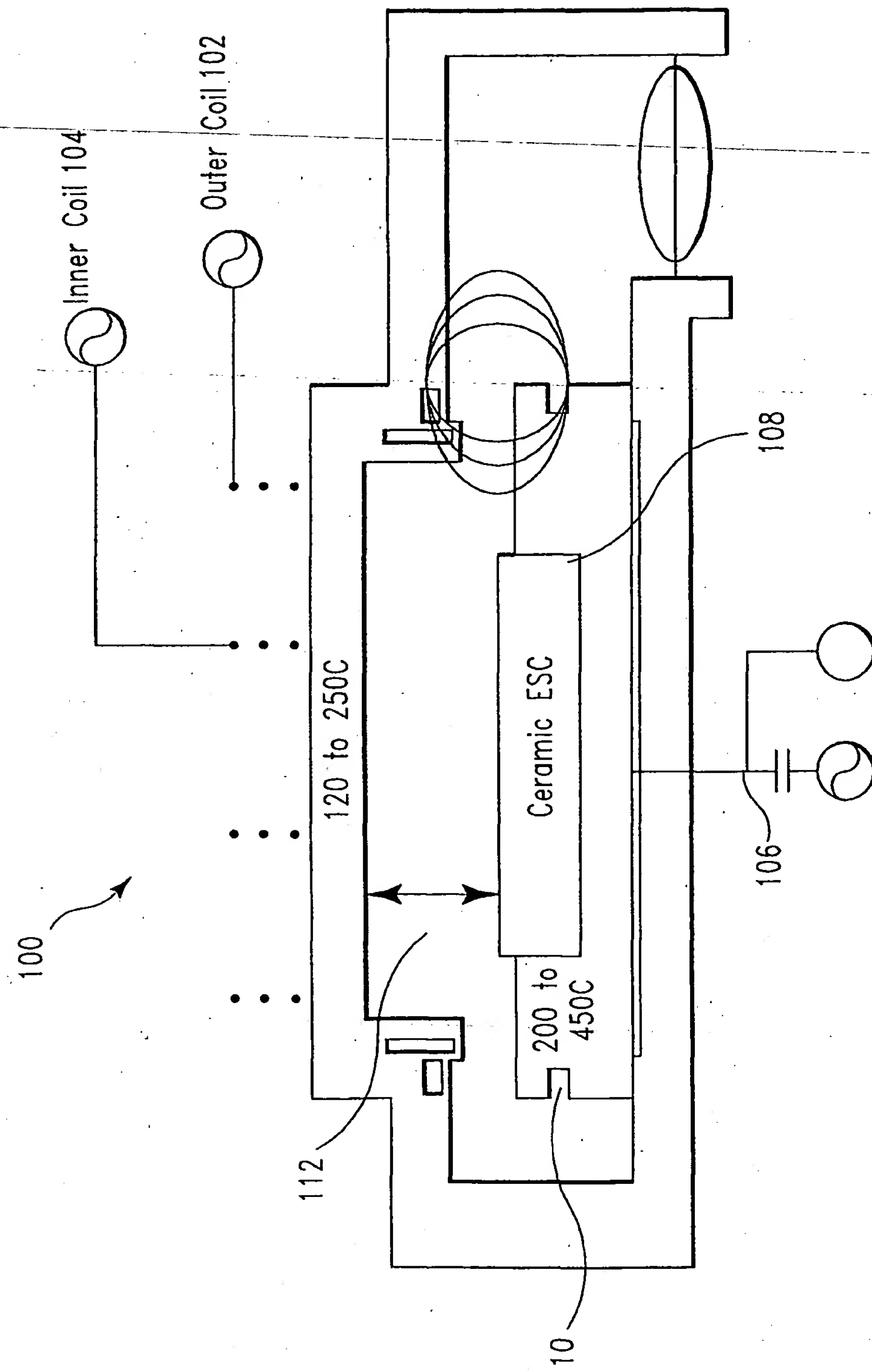
Inner Coil 104
Outer Coil 102
108
Ceramic ESC
120 to 250C
200 to 450C
106
100
112
110

FIG. 1

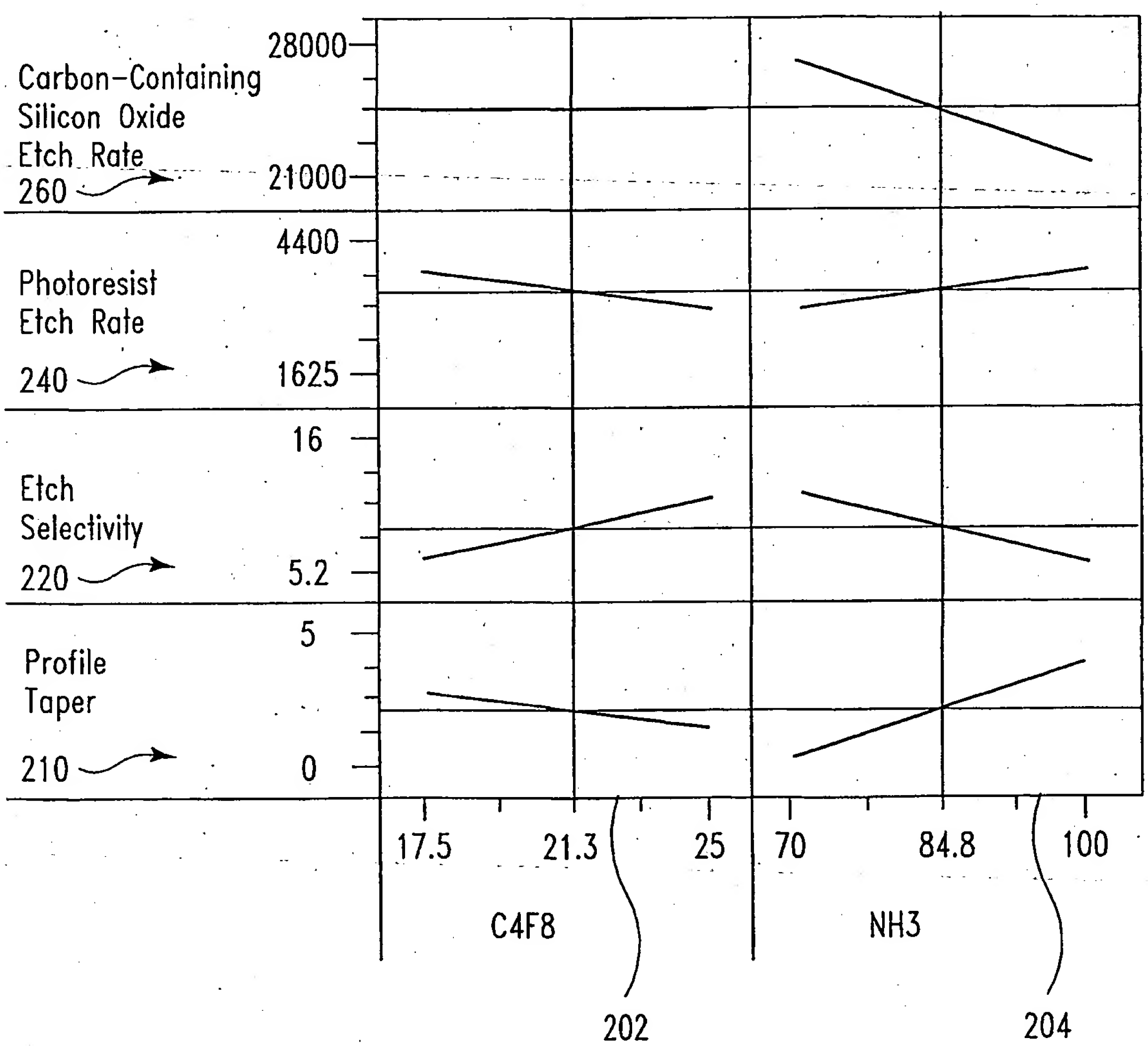
Carbon-Containing Silicon Oxide Etch Rate
260
28000
21000
Photoresist Etch Rate
240
4400
1625
Etch Selectivity
220
16
5.2
Profile Taper
210
5
0
17.5
21.3
25
70
84.8
100
C4F8
NH3
202
204

FIG. 2